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Effects of 80 MEV Electron Damage on Thermal Properties of Polystyrene.

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ABSTRACT

Measurements of the thermal conductivity of polystyrene, irradiated with 80 Mev electrons, were made in the temperature range of 1.0°K to 5.0°K. Additionally, an estimate of the corresponding heat capacities was made. Samples irradiated received total doses of approximately 70, 200, 230, 550, and 1120 M rads.

There was no observable effect, due to radiation induced crosslinks, on the thermal conductivity. The heat capacity, however, showed a marked decrease with increased dose. This effect is attributed to a reduction in the "excess" heat capacity of polystyrene, indicating that crosslinking has its greatest effect on the loosely bound polymer segments.

Polymer characterization was accomplished by use of intrinsic viscosity and equilibrium swelling techniques.

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I. INTRODUCTION

The purpose of this investigation was to study the effects of radiation induced crosslinking on the thermal properties of an amorphous polymer. In this study measurements of the thermal conductivity and heat capacity of polystyrene subjected to 80 Mev electron irradiation were made in the liquid helium temperature range.

This investigation was motivated by the fact that in view of current understanding of thermal phenomena in amorphous substances the expected result could not be predicted with certainty. It was hoped that these studies might elucidate the specific role of crosslinking on the low temperature thermal properties of amorphous substances. Further, from a purely technical point of view, these materials are good thermal insulators, and it was desired to find if they could be expected to maintain this property in the presence of a radiation environment.

Radiation Effects on Polymers

Two major effects are observed upon irradiation of polymers; degradation and crosslinking. These processes are essentially the reverse of one another, the first being the breaking of covalent bonds and the second, the formation of extra covalent bonds, and may occur simultaneously in a given polymer. In spite of the possibility of competing effects, one process generally predominates leading to the broad categorization of polymers into two classes, those which degrade and

those which crosslink. Degradation involves the breaking of bonds along the polymer chain resulting in a reduction of the polymer average molecular weight. Since this effect was not of direct interest in this investigation, further mention of degradation will be limited to specific problems as they directly relate to polystyrene.

The process of crosslinking, induced by ionizing radiation, involves the formation of covalent bonds between polymer chains. This results in an increase in the average molecular weight of the polymer and under high degrees of crosslinking will lead to the formation of a three dimensional network. The mechanism of crosslinking is not understood, but it is generally agreed that the production of free radicals, ions, and molecular excitations, induced by the incident radiation, all play some part in crosslinking. Efforts to explain all the experimental observations in terms of a general, all inclusive theory, have not been successful. The theories fall into two general classes. The first class suggests that a single event (ionization or excitation) is associated with each crosslink. The formation of a crosslink would then be related to direct or indirect action of the excited entity with a neighboring polymer unit. The second class of theories requires two separate and independent events, the first an excitation process resulting in a mobile ~~reaical~~ radical which may move along and/or between polymer chains until two or more excited units are in close proximity at which time they interact to form a crosslink.

Numerous specific reaction mechanisms have been postulated to support these proposals, and considerable experimental evidence is

available to indicate that either concept may be correct in specific cases. However, there is sufficient conflict in the results to prohibit definite conclusions concerning the general applicability of the two models. Fortunately, knowledge of the exact crosslinking mechanism is not essential to this investigation.

A number of factors must be considered when irradiating polymers to insure the production of the events of interest and to minimize the occurrence of secondary effects. Factors which have been considered for polystyrene are: (1) dose and dose rate (2) oxidative degradation and (3) temperature effects. The relationship of dose rate and total dose to the extent of damage in polymers has received considerable attention. In the case of crosslinking of polystyrene, Charlesby [1] has shown that the degree of crosslinking is independent of dose rate and a function of total dose only. In the same series of experiments it was shown that degradation in polystyrene does not occur as a direct result of ionizing radiation. A number of investigators have observed degradation in polystyrene when samples, having a large surface area to volume ratios, were irradiated in air. This is thought to be the result of oxidative degradation and the effect may be minimized by irradiation in vacuo and/or by judicious choice of sample geometry. A series of experiments was conducted by Alexander & Toms [2] using 1/2" rods and thin films of polystyrene. The amount of crosslinking in each sample was compared by determining the amount of the gel formed when samples were dissolved in an appropriate solvent. The

effect of oxidative degradation in the polystyrene rods was found to be considerably smaller than for the thin films. Additionally, the degradation in the rods appeared to saturate at moderately low doses.

The effect of temperature on the degree of crosslink formation in polystyrene has been studied by Pravendnikov et al[3]. Two factors related to temperature, significant to this investigation, were noted. The first being an increase of approximately 50% in the degree of crosslinking when a sample of polystyrene irradiated at 25°C was heated above the glass temperature. This effect is assumed to be related to an increased mobility of free radicals which were trapped at lower temperatures. Secondly, a drastic reduction in the efficiency of crosslink formation was observed for specimens irradiated at 130 to 140° C. This effect has been interpreted by the assumption that at these high temperatures the radicals reacted primarily by disproportionation instead of combining.

In the study of radiation effects on materials it is necessary to have a quantitative method of describing the extent to which various effects occur. For polymers, as in radiation chemistry, this description is in terms of an appropriate G-factor. The G-factor for a specific effect is the number of events produced per 100 ev of energy deposited in the sample. G-factors have been experimentally determined for numerous processes (i.e., crosslinking, degradation, gas evolution) in many polymers. Obviously the G-factor of particular interest here is for crosslinking in polystyrene. For crosslinking in polystyrene Charlesby [1] reports $G = 0.05 \pm 0.01$. This value has been used throughout this

investigation. It is worth restating that the extent of crosslinking in polystyrene is independent of dose rate and that the G-factor of 0.05 ± 0.01 has been established over a 10^5 range of radiation intensities [1]. It is interesting to note that $G_{c.l.} = 0.05$ is relatively low compared to many other linear polymers, which typically have G-factors as high as 5.0. The reduction in G-factor for polystyrene is explained by the "sponge" effect. This effect is associated with the benzene ring in polystyrene. It has been shown [1] that the benzene ring is capable of absorbing considerable excitation energy from the linear part of the polystyrene chain. This energy resides in the resonance structure of the double bonds of the benzene ring. Due to the numerous states associated with these resonances the benzene ring is able to dissipate the energy without causing ionization or free radical formation. Hence the small crosslinking G-factor for polystyrene.

The G-factor allows a convenient description of radiation change, demonstrated, for example, by the relation between total dose and molecular weight between crosslinks

$$M_c = \frac{.48 \times 10^6}{G\ r} \qquad (1)$$

where M_c = average molecular weight between crosslinks

r = Dose in M rads

Equation (1) has been developed [1] based on the statistical considerations assuming random distribution of crosslinks. M_c gives a measure of the average distance between crosslinks along a single chain. The

importance of this factor to this investigation will become apparent in later discussion.

Another quantity defined in polymer studies which is important to this work is the crosslinking coefficient δ . The crosslinking coefficient is related to the initial Molecular weight and defined as

$$\delta = \frac{M_w}{M_c} \qquad (2)$$

When δ = 1 the polymer has just sufficient crosslinks to cause gel formation (i.e., the formation of a three dimensional network). As the number of crosslinks increases the amount of gel formed becomes greater. Recognizing this requirement for incipient gel formation it is a simple matter, by using equation (2), to determine the dose required to reach the gel point for a given polymer.

Selection of Polystyrene

The choice of polystyrene as the material to be studied was based on a number of considerations. From the statement of the purpose of the investigation, it is clear that an amorphous polymer which crosslinks upon irradiation was required. Additional factors considered were (1) side effects and competing degradation, (2) glass temperature of polymer, (3) induced radio activity, and (4) extent and accuracy of existing data for the material selected.

The problem of extensive side effects and competing degradation was found to be minor in the case of polystyrene. As mentioned previously degradation in polystyrene is certainly insignificant and

may be non-existent.

The production of gaseous by-products has been noted, with H_2 being the major product. The G-factor for H_2 production has been reported by Wall and Brown [4] as between .03 and .04. This indicates that the amount of H_2 generated would be small, and of no consequence in this study. Other polymers, particularly the acrylonitriles were discarded from consideration because of the generation of toxic gases upon irradiation.

Polymer glass temperature was considered for a number of reasons. It was desirable to use a material with a high glass temperature so as to minimize the problems encountered in handling and machining. Further, as pointed out earlier for polystyrene, the cross-linking G-factor may be drastically effected at the glass temperature. Consequently, it was desirable to select a polymer with a high glass temperature. This choice would minimize the precautions necessary in handling the sample, particularly with regard to temperature control during and after irradiation.

The possibility of induced radio activity had to be considered since the sample was to be placed in an electron beam. A number of possible nuclear reactions, involving the major constituents of polymers (i.e., C, H,), were considered and none was found to lead to any long-lived radio isotope. In order to minimize preliminary work and ancillary experiments a material with established low temperature properties was highly desirable.

Polystyrene was found to satisfy all the desirable characteristics required for a sample.

Thermal Conductivity of Amorphous Materials

A theory of the thermal conductivity of amorphous substances has been proposed by P. G. Klemens [5] . According to this theory, thermal conductivity is determined by the scattering of phonons by the disordered molecular structure of the substance. Application of the idea of structural scattering and the Debye continuum model for vibrational spectrum led Klemens to an expression for thermal conductivity at very low temperatures

$$K = \frac{3.29k^2T}{3\pi h}\left[\frac{A}{a} + \frac{2B}{a}\right] \qquad (3)$$

where k is Boltzmann's constant, T is the absolute temperature, h is Planck's constant, A and B are dimensionless constants characteristic of the substance, and a is a typical distance between vibrating units.

In this development Klemens assumed that when phonon wavelengths were on the order of or less than the elastic correlation length, the phonon mean free path should be constant and should be equal to Aa and Ba for longitudinal and transverse modes, respectively. On the other hand, for phonon wavelengths much greater than the correlation length, Klemens showed that the mean free path would be proportional to the square of the wavelength of the phonon. These mean free paths are given as $\frac{A}{a}\lambda^2$ for longitudinal waves and $\frac{B}{a}\lambda^2$ for transverse waves. The dependence of mean free path on wavelength in this case

arises from the ability of phonons with long wavelengths to average over the disorder.

Klemens applied his theory to the explanation of results obtained by R. Berman on low temperature thermal conductivity measurements on quartz glass [6]. Klemens concluded that for amorphous substances A is characteristically much greater than B and that, consequently, the transverse mode is much more effectively scattered than the longitudinal mode. The contribution of the transverse mode to thermal conductivity should then be unimportant at very low temperatures where phonon wavelengths are large and of the order of or larger than the correlation length.

Klemens further showed that not only was heat transport limited to longitudinal modes at low temperatures, but that at any but very low temperatures the mean free path for this mode was limited by conversion of longitudinal waves to transverse waves which are subsequently equiliberated rapidly. He found this important process to be dependent on temperature and characterized it by a function, $f(T/T_o)$, where T_o is a paramerter with dimensions of temperature. Klemens wrote the contribution from the longitudinal mode to thermal conductivity as

$$K_L = \frac{k^2 A T}{3\pi h a} \left[f(T/T_o) \right] \qquad (4)$$

where $f(T/T_o)$ is a tabulated integral [7], having a value of 3.29 for $T/T_o = 0$. As the temperature increases, $f(T/T_o)$ rapidly decreases giving rise to a greater contribution to the thermal conductivity by transverse modes of propagation.

The linear dependence of thermal conductivity at low temperatures can be seen from equation (4). The linear dependence at low temperatures can also be seen by noting that the phonon mean free path, given by $\frac{A}{a}\lambda^2$, yields an average mean free path inversely proportional to the square of the temperature. Applying this fact together with a continuum model which gives a heat capacity proportional to T^3 in the kinetic theory result for thermal conductivity, $K = \frac{1}{3} CS\Lambda \propto T^3(\frac{1}{T^2})$, one sees the linear dependence of K on T.

Although Klemens' theory was developed to fit the data obtained from measurements on quartz glass, W. Reese [8] has shown that by using reasonable values for A/a and T_o, namely, $1.21 \times 10^9 cm^{-1}$ and 6.0° K, respectively, one could fit Klemens' theory reasonably well to low temperature thermal conductivity data for polystyrene. Thus it appears that in the main, Klemens' theory adequately explains the thermal properties of amorphous polymers.

Applying Klemens' theory and the foregoing value for A/a one finds from the geometry of the polystyrene structure and polymer density that a is of the order of 10^{-7} cm so that Aa is about 1.2×10^{-5} cm. The phonon wave length for a mean temperature in the 1° K to 5° K range would be approximately 2.4×10^{-6} cm, thus giving a mean free path of about 7×10^{-3} cm, if we take $\Lambda = \frac{A}{a}\lambda^2$; of course this is a bit of an overestimation since $\lambda < Aa$. The initial irradiation of Sample I produced crosslinks at about every 4×10^{-5} cm along the polymer chain while the total accumulative dose in the sample produced crosslinks at intervals of about 1.75×10^{-6} cm. Thus one can easily introduce

crosslinks at distances which are short compared with other lengths involved in the problem, leading to the hope that one can introduce meaningful amounts of damage for investigative purposes.

One cannot directly apply Klemens' theory to predict the effect of crosslink formation within a polymer on its thermal properties. Any previous study or measurement of the effects of crosslinks is unknown. However, one might make some simple qualitative remarks on the possible effect of crosslinks using ideas similar to those of Klemens. Very crudely, a crosslink might be viewed as a severe perturbation on the elastic properties of the polymer thereby providing for additional scattering and a decreased phonon mean free path. This effect would be observed as a decrease in the thermal conductivity. However, one might also look at crosslinks as being mere point imperfections within the structure of the polymer. These local imperfections might represent little or no inhomogenity to the advancing phonons whose wavelengths in the temperature range of $1^{\circ}K$ to $5^{\circ}K$ are very large relative to the size of the crosslink itself. The wave, therefore, might merely diffract around these obstacles thereby reducing any scattering capability of the crosslinks to negligible proportions.

In summary, Klemens' theory has been successfully applied to explain thermal properties of amorphous polymers, but its application in predicting the effects of crosslinks within an amorphous polymer is not readily apparent. It was hoped that experimental data taken for irradiated polymers might provide further insight to the applicability of the theory to explain thermal transport phenomena.

II. EXPERIMENTAL CONSIDERATIONS

General Procedure

For the experiment a sample of about 7 centimeters in length was cut from a 1.30 cm diameter rod of polystyrene manufactured by Cadillac Plastics and Chemical Company. The sample, prepared for experiment, was mounted in a low temperature experimental apparatus and its thermal conductivity was determined by methods to be discussed later.

The sample was then irradiated four successive times with a linear accelerator using approximately 80 MeV electrons to accumulative doses of about 70, 230, 550, and 1120 Mrads. For each dosage level the thermal conductivity of the polystyrene sample was determined for 14 temperature points in the range of 1° K to 5° K. A small specimen was removed from the end of the sample after each irradiation to permit determination of crosslinking density in the polymer for each dose.

Due to an anomaly in the thermal properties of the sample observed following the second irradiation, this dosage level was re-examined. For this purpose a second sample, cut from the same stock as the original, was irradiated to a comparable dose and its thermal conductivity was determined. A discussion of the anomalous result is included in this paper. The original sample is designated Sample I hereafter, and the second sample is referred to as Sample II.

Sample Irradiation

The polystyrene samples were irradiated by an electron beam produced by the NPGS linear accelerator. The samples were irradiated end-on, the impinging electron beam being directed along the axis of the cylindrical sample. During the first two irradiations of Sample I, the shape of the cross-section of the electron beam was approximately elliptical having dimensions 3/8" x 1/2". The beam subsequently used was of circular cross-section, 1/4" in diameter. Throughout the irradiations the beam was very well defined as evidenced by observation of a fluorescent screen placed on the face of the sample. This technique of sensing, plus reasonably accurate sample axial allignment, insured that the electron beam, in the main, passed through the sample.

The exact variation of electron density over the cross-section of the beam was unknown. However, the pattern of brightness on the impact screen indicated that the density of the beam was greatest at the center of the cross-section. Since the cross-section of the beam was generally smaller than the face of the sample, the beam was steered across the sample face in an effort to produce a more uniform irradiation of the sample.

Measurements of the current passing through the sample were obtained using a Faraday cup current collector which was situated approximately one foot behind the sample. The window of the device was three inches in diameter. Current values measured in this manner varied from .15 to .50 μamps. Total integrated current flux through

the sample was measured using an Eldorado Electronics current integrator (Mode C1-110). Electron energies were constant for any single irradiation of the sample, but varied from 80 to 88 MeV from one irradiation to another. Table I contains data relative to the irradiation of the samples.

The total energy absorbed by the sample is given by the product of the total number of electrons passing through the sample and the amount of energy desposited per electron passing through. The energy deposited per electron is given by the mass absorption coefficient and the density. The energy deposited, when stated in units of 100 ergs per gram of sample, gives the irradiation dose in rads.

The values of mass absorption coefficient of polystyrene for electrons, which are dependent upon the energy of the incident particle, were taken from the work of Berger and Seltzer [9]. The coefficients used neglect any energy absorption due to the creation of Bremsstrahlung radiation. The relatively small lateral dimensions of the sample in its irradiating configuration precluded significant absorption of gamma radiation which originates from the Bremsstrahlung effect. Thus, it was assumed that all energy lost from the beam due to Bremsstrahlung production escaped from the sample.

Subsequent to the completion of all irradiations, some doubt was cast on the validity of the current values measured by the Faraday cup. Measurement of typical currents from the linear accelerator by a secondary emission monitor indicated that the actual current might be considerably larger than that measured by the Faraday cup. However,

Sample*	Sample Length (cm)	Beam Current (μamps)	Irradiation Duration (min)	Total Flux (μcoul)	Electron Energy (MeV)	Mass Absorption Coeff(cm^2/g)	Dose (Mrad)	Accum Dose (Mrad)
I-1	6.970	.18 - .20	39	420	80	2.117	66.9	66.9
I-2	6.765	.20 - .25	66	1000	83	2.120	159.5	226.4
I-3	6.515	.40 - .50	65	2000	85	2.122	319.4	545.8
I-4	6.037	.20 - .40	77	1595	80	2.117	254.1	
		.15 - .24	120	2000	88	2.124	319.7	1119.6
II-1	7.050	.30 - .50	53	1200	83	2.120	191.5	191.5

* I-1 refers to 1st irradiation of Sample I, ect.

Table I

Sample Irradiation Data

no additional means was available to corroborate this supposition or to precisely determine the magnitude of the error.* Even though an uncertainty of current values exists, it should be pointed out that the dose rates calculated from the current values as measured by the Faraday cup are generally consistent with the dose rates necessary to give the amount of crosslinking actually obtained in the sample. The crosslink density in the sample was independently determined using polymer swelling techniques. These techniques, as well as a discussion of the results of their application, are presented subsequently.

Temperature Control During Irradiation

To meet the requirement of keeping the sample below the softening temperature, 80°C, provisions were made to cool the sample during irradiation. A collar of .04" aluminum sheeting was wrapped tightly around the entire length of the sample. Extensions of the ends of the collar were immersed in a liquid nitrogen bath during irradiation. The collar was insulated against heat loss to the air by a covering of styrofoam.

The cooling device when used with a polystyrene sample containing a thermocouple located on the sample axis was able to cool the sample to 150°K. Under maximum irradiating current of .5 μamps, the power dissipated per centimeter of sample length would be approximately 1 watt. Assuming that this heat is generated uniformly along the length

*Recent current measurements using calorimetric techniques tend to agree with SEM measurements. See Appendix C.

of the centimeter and that it flows radially to the surface of the sample, we find

$$T(R) = T(O) - \frac{\dot{Q}}{4\pi K} \qquad (5)$$

where T(R) and T(O) are the temperatures of the surface and center of the rod respectively; $\dot{Q}$ is the power dissipated per centimeter of length, and K is the average thermal conductivity of polystyrene over the appropriate temperature range, approximately 1.30 mwatt/ cm--^{o}K. From this we find the maximum temperature to which the center of the sample might rise is about -65^{o}C, well below the softening temperature of 80^{o}C for polystyrene. Although the calculation is somewhat artificial, the difference of 145^{o} appears to provide a very adequate safety margin against a rise of sample to undesirably high temperatures.*

Some Observations of the Irradiated Sample

It was noted that both samples, which were originally colorless, turned yellowish-brown after the initial irradiation. Sample I became darker in color with each succeeding irradiation. This coloration may be related to reactive entities such as free radicals or unsaturated compounds formed within the polymer during irradiation [1]. However, the mechanism by which the discoloration occurs is unknown. After several weeks, the coloring of the samples appeared to have faded slightly. It was noted that the fading appeared to progress from the

*See Appendix C for effect of increased beam intensity.

surface inward which would indicate that some reaction might be occuring between oxygen diffusing into the sample and reactive entities responsible for the coloration. However, this theory has been previously questioned [1].

Following the fourth irradiation of Sample I, a persistent spiral pattern of dark substance was noted within the sample. The formation of this substance was heaviest in the sample end through which the electron beam entered. It is speculated that the substance might be elemental carbon formation resulting from some collision phenomena.

The sizes of the samples were measured after each irradiation. The dimensions of the samples were not changed within experimental error by the resulting crosslink formation.

Characterization of Polymer Sample

During the course of this investigation it was necessary to determine various properties of the sample. Two properties of particular interest were the weight average molecular weight (W.A.M.W.) of the unirradiated sample and the degree of crosslinking resulting from each irradiation. The weight average molecular weight was necessary to permit calculations of the gel dose required for the sample. Additionally, the W.A.M.W. was used to estimate the degree of crosslinking by G-factor calculations. A method for determining the degree of crosslinking independent of G-factor calculations was desirable in order to provide a check against computations based on the Linear acceleator instrumentation and to further verify that values of the G-factor obtained using low energy

neutrons and electrons are also valid for ultra-relativistic electrons. The methods used to determine molecular weight and degree of cross-linking were intrinsic viscosity and equilibrium swelling.

In all theoretical, as well as experimental, considerations concerning polymers it is essential to consider that there exists a molecular weight distribution rather than a unique chain length. Charlesby [10] shows that the molecular weight of commercial polystyrene follows a random distribution. Based on these findings it was assumed that the samples used in this investigation possessed a random distribution of molecular weight.

Practically all polymer characterization techniques involve a solvent polymer system. Because there was considerable data available for benzene-polystyrene systems, benzene was chosen as the solvent for these determinations.

Molecular Weight Determination

W.A.M.W. determinations for polystyrene were based on intrinsic viscosity techniques [11] . Intrinsic viscosity (limiting viscosity number) is defined as

$$[\eta]_o = \lim_{c \to 0} \frac{\eta - \eta_o}{c\,\eta_o} \qquad (6)$$

where

$[\eta]_o$ = intrinsic viscosity (LVN)
η_o = viscosity of solvent
η = viscosity of polymer solution
c = concentration of polymer solution in gm/100 ml

An empirical relation between intrinsic viscosity and M_η (Viscosity Average Molecular Weight) has been developed

$$[\eta] = K M_\eta^a \qquad (7)$$

where K and a are temperature dependent constants of the polymer-solvent system. Equation (7) applies to polymers of uniform molecular weight distribution. For a random distribution it can be shown that $M_\eta = M_n \left\{ (a+1) \Gamma (a+1) \right\}^{1/a}$ and also that $M_n = \frac{M_w}{2}$ [1], so that the weight average molecular weight for a random distribution is:

$$M_w = \frac{2 M_\eta}{\left\{ (a+1) \Gamma (a+1) \right\}^{1/a}} \qquad (8)$$

For the polystyrene-benzene system a = .74 [12] so that

$$M_w = \frac{2 M_\eta}{1.87} \qquad (9)$$

Viscosity measurements of a polystyrene-benzene solution were made using a Cannon-Fenske Capillary viscometer. Viscosity is related to flow time by:

$$\frac{\eta}{\rho} = At + \frac{B}{t} \qquad (10)$$

where η = solution viscosity
ρ = solution density
t = flow time

The constants A and B are characteristic of the viscometer and were determined by calibration with H_2O. Since the variation of ρ for each concentration checked was small the value of $\frac{\eta}{\rho}$ from equation

(10) was substituted directly into equation (6), to determine $[\eta]_c$. The value of $[\eta]_o$ was obtained graphically by plotting $[\eta]_c$ vs. C and taking the intercept at C = 0 as the value of $[\eta]_o$.

Experimental data relating $[\eta]_o$ to M_η for a polystyrene-benzene system was then used to determine the W.A.M.W. of the specimen [13]. The weight average molecular weight of the polystyrene used in this study was determined to be 192,500.

Crosslinking Determination

As mentioned previously polystyrene crosslinks when subjected to ionizing radiation yielding, when total dose is high enough, a three dimensional network. This network becomes insoluble in the usual solvents for polystyrene resulting in a gel fraction and a sol fraction for the irradiated sample. Additionally, the gel fraction swells due to entrapment of solvent molecules. The extent of equilibrium swelling has been related thermodynamically to the molecular weight between crosslinks in the following equation [14]:

$$\ln(1-\chi) + \chi + \mu\chi^2 + \frac{\rho V}{M_c}\left(\chi^{1/3} - \frac{\chi}{2}\right) = 0 \qquad (11)$$

where
- χ = Polymer volume fraction of swollen gel
- μ = interaction parameter
- ρ = polymer density
- V = molar volume of the solvent
- M_c = average molecular weight between crosslinks

If the degree of swelling is large (x small), equation (11) may be simplified as

$$(0.5 - \mu) x^2 = \frac{\rho \nu x^{1/3}}{M_c} \tag{12}$$

or substituting $V = \frac{1}{x}$

$$V^{5/3} = (0.5 - \mu) M_c / \rho \nu \tag{13}$$

When applying this approximation it is necessary to keep in mind the conditions which lead to this relation. Reasonable results will be obtained for high swelling ratios, but the equation will be invalid when V approaches 2 or 3. Further, this relation fails near the gel point where the gel fraction varies rapidly with dose. Corrections may be applied to the results near the gel point which lead to fair agreement with equation (13).

These corrections involve:

(1) correction for large sol fraction.

(2) corrections for crosslinks required for gel formation before a closed network is obtained.

Further substitution in equation (13) for M_c in terms of G-factor and dose leads to

$$V^{5/3} = \frac{.48 \times 10^6 (.5 - \mu)}{\rho \nu r G} \tag{14}$$

From equation (14) it is apparent that a plot of log r vs. log V should result in a straight line with slope - 0.6.

It is customary in swelling determinations to substitute a weight ratio in place of the volume ratio V, that is the ratio of the gel plus imbibed solvent weight to the initial weight of the sample.

The use of the weight ratio for V is desirable because of the relative ease of obtaining weights compared to volumes. In order to compare results of this investigation with reported data, this approach was used throughout.

The technique used for determining the gel fraction and swelling ratio for irradiated samples was essentially that described by Allen [11]. A .2 g sample of irradiated polystyrene was placed in approximately 25 ml of benzene, and allowed to stand for a minimum of 24 hours. After draining the sol fraction, the swollen gel was placed in a benzene atmosphere for 48 hours. The imbibed solvent was removed by vacuum drying after the swollen gel was weighed. During the solvent removal the temperature was kept below the polystyrene glass temperature. The data obtained was used directly in equations (2) and (13) to determine crosslinking densities and average molecular weight between crosslinks.

The results of the swelling determinations of M_c together with values of M_c computed from equation (13) are listed in Table II. The comparison of the values of M_c indicates good correlation except for the most heavily irradiated sample. This discrepancy is due, at least in part, to two factors. First, the time allowed for solution of the sol fraction (24 hours) was probably insufficient to leach out all of the uncrosslinked polymers. This effect would be most severe for the most heavily radiated sample due to the extensive hindrance presented by the crosslinked network to movement of the soluble polymer molecules. This would result in a greater value of V than would be appropriate and consequently lead to large values of M_c. Secondly, as shown by

Sample	Irradiation	Calculated[1] Dose M rads	M_c	Swelling[2] V	M_c	$\frac{M_c \text{ swelling}}{M_c \text{ G-Factor}}$	δ_S	δ_G	% Sol
I	1	66.9	143,490	22.2	136,576	.952	1.41	1.34	83.75
	2	226.4	42,402	11.31	44,232	1.04	4.35	4.52	51.12
				12.4	43,495	1.03	4.43	4.56	58.3
	3	545.8	17,588	6.19	16,141	.918	11.93	10.94	4.17
	4	1119.6	8,574	7.63 7.31	22,116	2.57	8.70	22.45	≈0.00
II	1	191.5	50,130	13.72	60,916	1.23	3.16	3.84	13.77

Table II

COMPARISON OF RESULTS OF SWELLING DETERMINATION WITH DIRECT CALCULATIONS

1 G = .05

2 μ = .41

Charlesby [15], the swelling ratio deviates from the straight line approximation for highly crosslinked systems. Both of these effects would result in displacing the experimental value of the swelling ratio above the approximation of equation (13). A high swelling ratio will result in a value of M_c which is too high for the total dose applied.

Figure 1 shows the swelling data together with data reported by Charlesby [15]. The results are seen to be parallel with, but displaced from Charlesby's data. Neglecting the heaviest dose, the slope of the experimental line is -.602, in good agreement with the approximate swelling equation. The displacement of the experimental line is most probably due to the limited time allowed for solution of the gel fraction. It has been noted by Charlesby [15] that the swelling volume of the gel fraction of crosslinked polystyrene passes through a maximum after a few days. The short leaching time of 24 hours would effect the observed swelling ratios causing a shift of the results to the right.

Although the complications mentioned above are considerable, the most significant uncertainty is related to the value of the parameter μ. Reported values of μ for a polystyrene-benzene system range between .2 and .45 [16, 17]. The impact of the value of μ on the results is best seen by rearranging equation (13) as

$$M_c = \frac{\rho \nu \quad V^{5/3}}{(0.5 - \mu)}$$

It is apparent that slight variation of the value of μ, if it is near .5, will cause a considerable change in M_c. Because of the range of values reported for μ, an arbitrary selection can be made to give the experimental

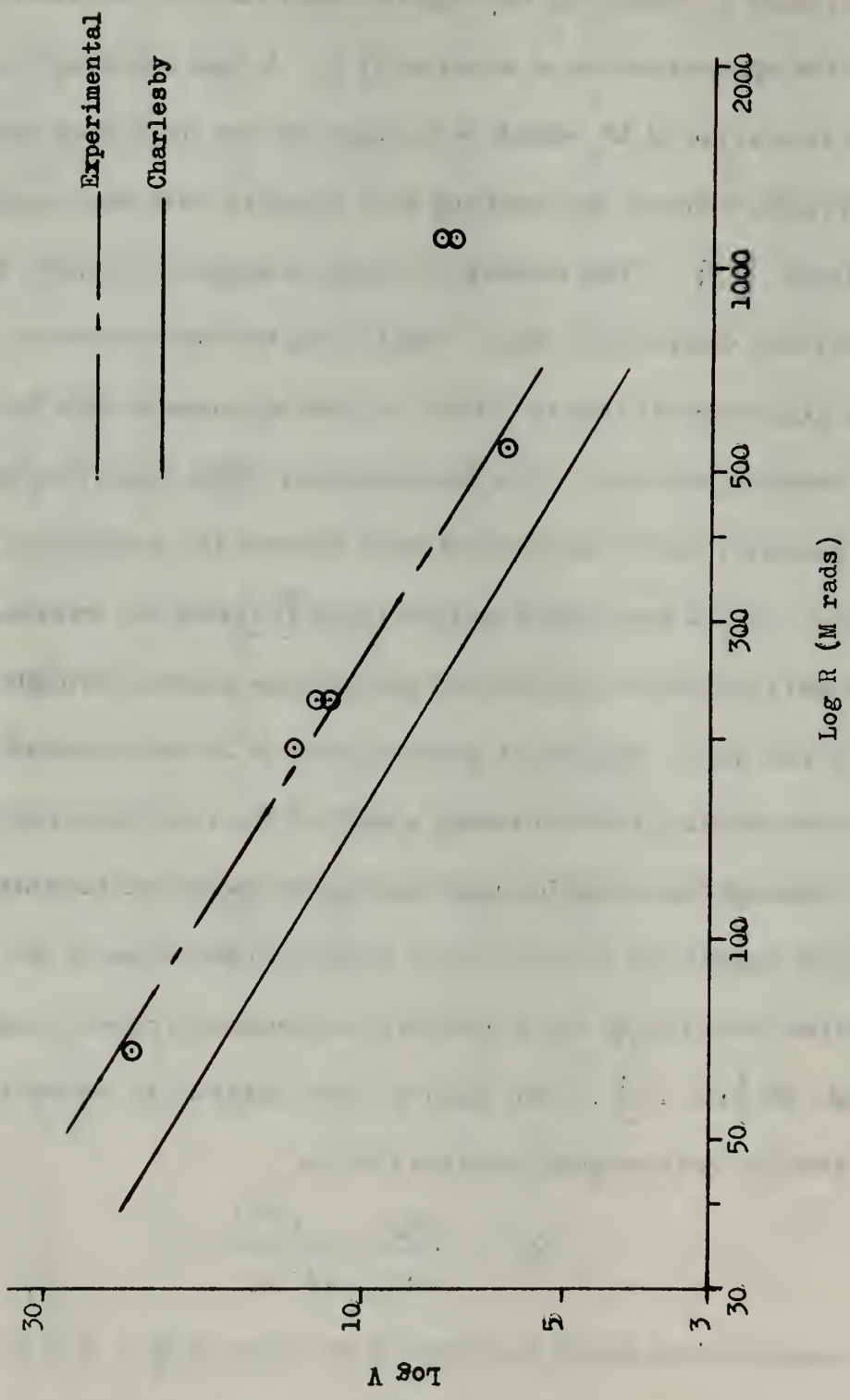

Figure 1. Swelling Ratio vs. Log Dose

results any value desired. The comparison of values of M_c in Table II are based on a value of $\mu = .41$[3]. Since the crosslinking G-factor for polystyrene has been well established the degree of crosslinking based on computation is considered to be more reliable than the results obtained from swelling techniques.* This assumption is considered to be especially valid in light of the great uncertainty associated with μ.

An experimental estimate of the gel dose for this sample of 59.5 M rads was obtained from Figure 2, a plot of % sol vs. log dose. In spite of a lack of data near the gel point a crude estimate may be obtained since the shape of the curve, assuming a random molecular weight distribution, is known [10]. This value of the gel dose is approximately 20.2% larger than the gel dose of 49.4 M rads computed from equation (1) using the G-factor of .05. This difference in gel dose values is not disturbing considering the preceding discussion of the many uncertainties related to the accurate determination of the sol and gel fractions.

An especially puzzling result is associated with the sol fraction determined for the second irradiation of Sample I. As can be seen from Figure 2, the sol fraction is especially high and completely inconsistent with the other determinations. This determination was made on two separate pieces of polystyrene from the same sample. In each case the

*See Appendix C

[3]The selection of $\mu = .41$ was based on a comparison of M_c determined G-factor calculation and swelling determinations considered in conjunction with the gel dose determined independently from sol fractions. Using $\mu = .41$ resulted in reasonable agreement with each of the factors considered.

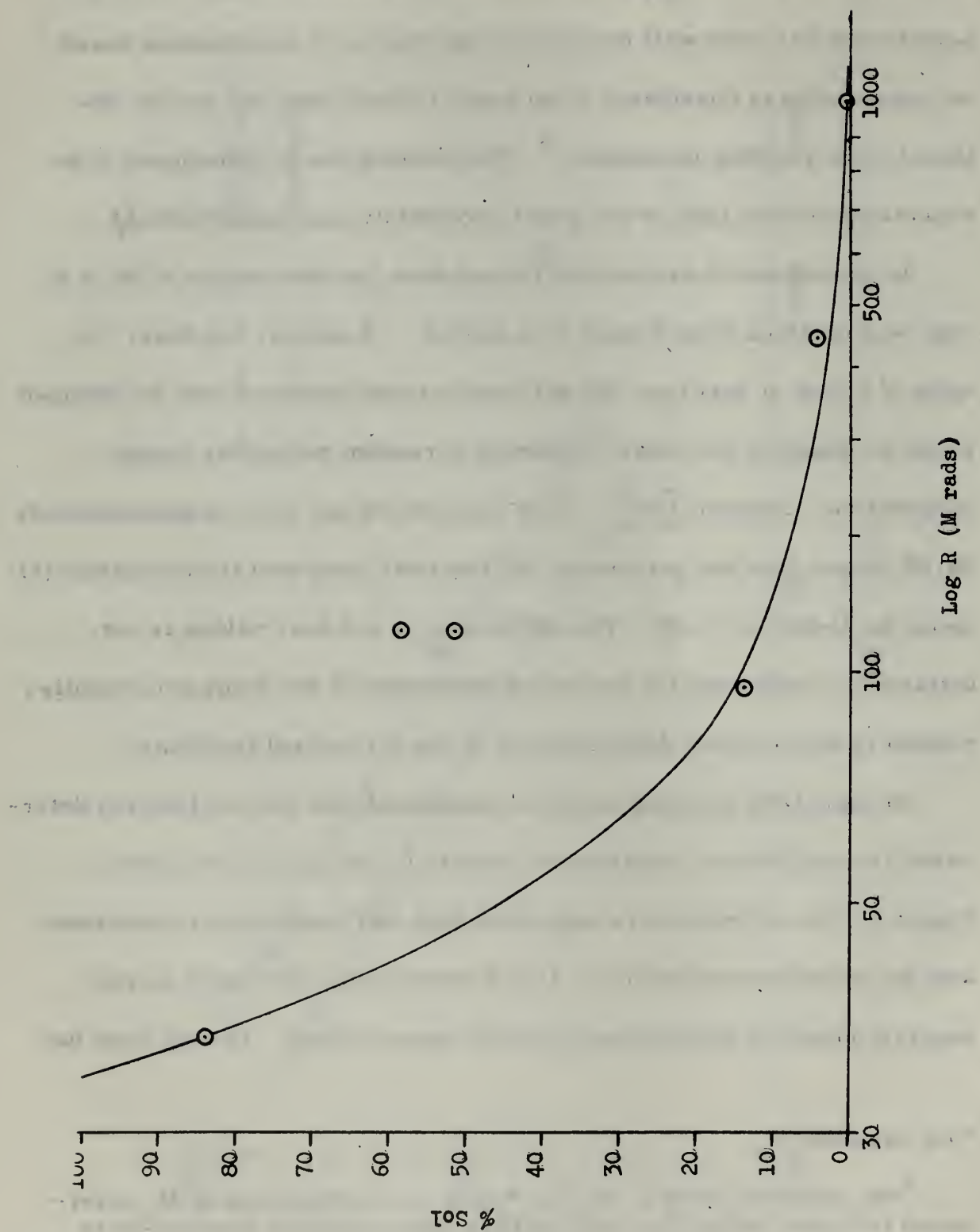

Figure 2. % Sol vs. Log Dose.

swelling data was consistent with samples from the other irradiations, but the sol fraction data was entirely anomalous. Efforts to explain this inconsistency in terms of non-uniform crosslinking failed. Consequently, we have no feasible explanation for this result.

Throughout this investigation, the G-factor for crosslinking in polystyrene due to irradiation with very high energy electrons has been accepted as .05. Certainly the possibility exists that the G-factor for this type of radiation is different from that associated with pile irradiation and low energy electrons. Unfortunately, the uncertainties association with the linear accelerator instrumentation and the limited number of samples available prohibited an investigation of this matter. Determination of the G-factor for high energy electrons, from sol fraction and swelling data might be a worthwhile investigation, when the instrumentation of the linear accelerator is completed.

Sample Preparation

Each of the two cylindrical samples were 1.30 cm in diameter and approximately 7 cm long. Two small holes were drilled through the center of the sample perpendicular to its long axis. These two holes, each approximately .1 cm in diameter and spaced about 4.5 cm apart, were drilled to hold leads for resistance thermometers. One end of each sample was tapped to accept a 1/4-20 threaded stud protruding from a copper block which was stabilized at that temperature at which the thermal conductivity was to be determined. Apiezon, type N grease, manufactured by Associated Electrical Industries, Ltd, was used to

insure good thermal contact between the sample and the copper block and between the sample and the thermal leads to the resistance thermometers.

Description of Apparatus

A diagram of the apparatus used to determine the thermal conductivity of the sample is shown in Figure 3. The significant function of each part was as follows. A large dewar (A) contained the liquid helium under vacuum to maintain a low environmental temperature of about 1.1° K. The shield heater (B) provided the heat to raise the temperature of the sample (C) from the bath temperature to that temperature at which the thermal conductivity of the sample was to be determined. The heater was wound around a collar shaped extension of the copper block (D) previously mentioned. The shield heater also provided heat to maintain the same temperature in the heat shield (E) as at the top of the sample. This inhibited radiation heat loss by the sample to its surroundings. The brass vacuum can (F), pumped to a vacuum of about 5×10^{-7} Torr, and the heat shield thus provided a means of thermally isolating the sample except for the controlled pathway via the copper block and a brass support tube (G). The vacuum can was sealed using an Indium 0-ring.

The sample and shield temperature was selected by adjustment of power to the shield heater to obtain a specific value of resistance of the Germanium resistor (H). The Ge resistor was used as a resistance thermometer. Its calibration against temperature will be discussed later.

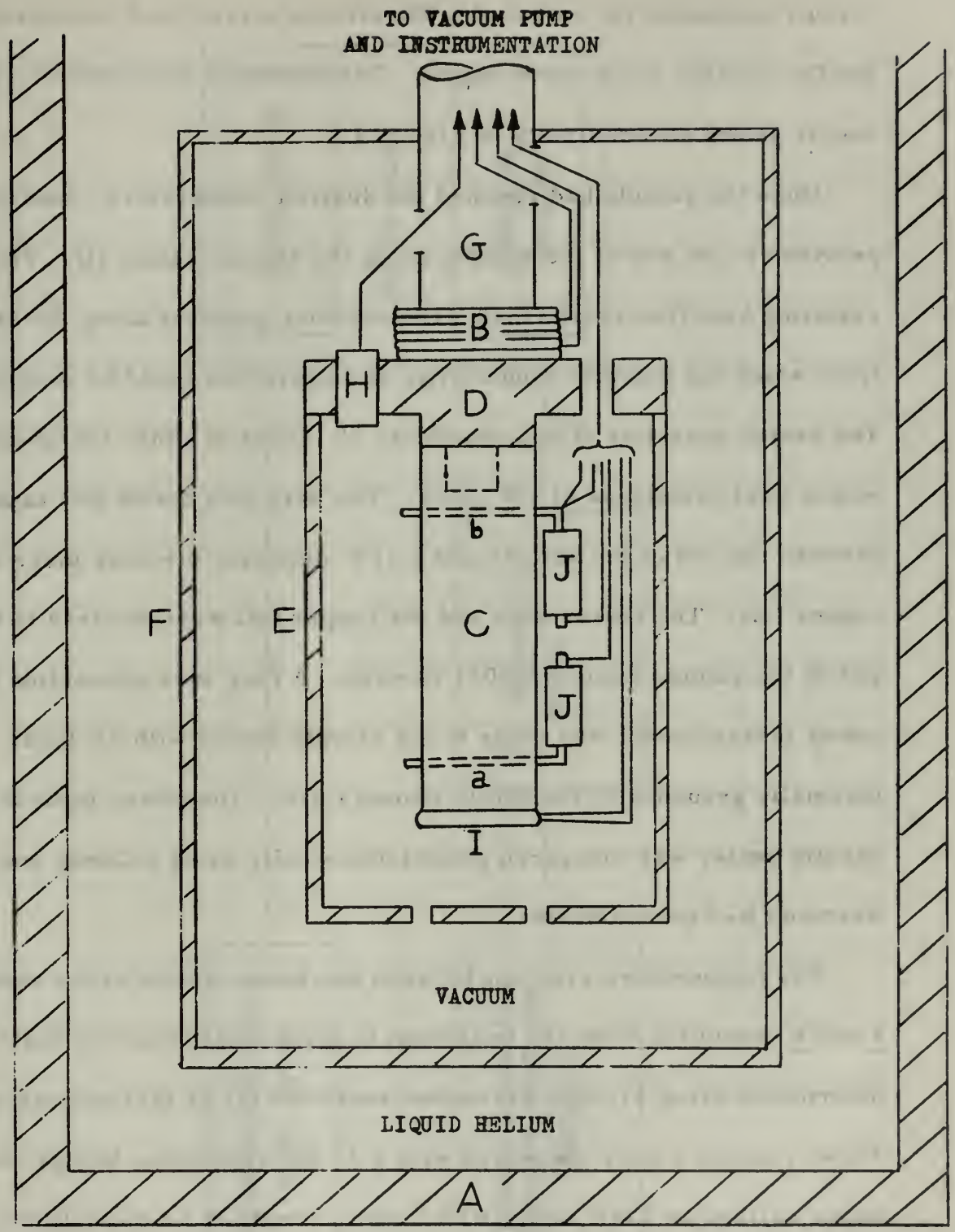

Figure 3. Apparatus for thermal conductivity determination at low temperatures.

The selected sample temperature was maintained using a servo-heating circuit employing the output of a Wheatstone bridge used to measure the Ge resistor as an error signal. The method of temperature regulation is shown schematically in Figure 4.

Once the sample had reached the desired temperature, heat was provided to the end of the sample using the sample heater (I). The resulting heat flow established a temperature gradient along the sample from which the thermal conductivity of polystyrene could be calculated. The heater consisted of approximately 15 inches of .002" manganin wire with a total resistance of 100 ohms. The wire was coiled and sandwiched between the end of the sample and a 1/2" diameter circular piece of thin copper foil. The heater wire and the copper foil were secured to the end of the sample using GE 7031 varnish. A four wire connection for power measurement was made to the sample heater with all leads thermally grounded to the shield temperature. The power input to the sample heater was measured potentiometrically using a Leeds and Northrup K-3 potentiometer.

The temperature gradient between two known points in the sample, a and b, resulting from the heat input to the sample from the heater, was determined using 47-ohm AB carbon resistors (J) as thermometers. These resistors were measured with a 37 Hz Wheatstone bridge circuit which utilized an EMC Model RJB lock-in amplifier as the null detector. The measuring circuit is shown schematically in Figure 5. Superconducting wire was used to interconnect the thermometers to insure that there was identical lead resistance for the two 47-ohm resistors

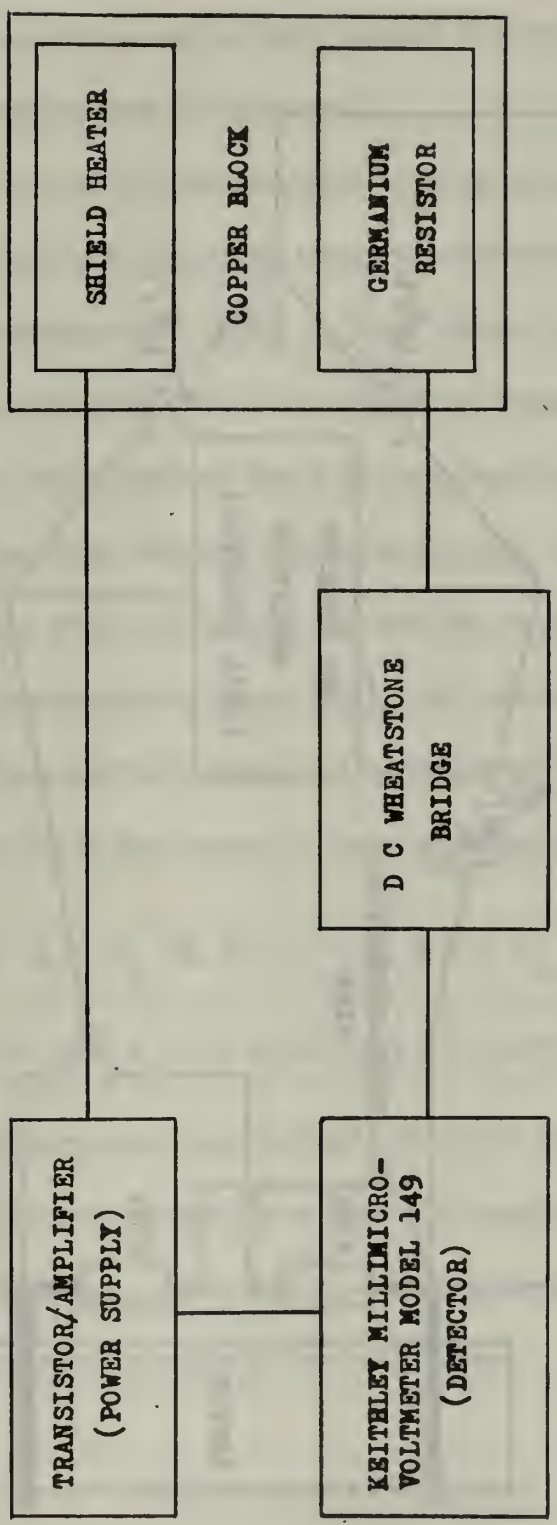

Figure 4. Sample and heat shield temperature regulation.

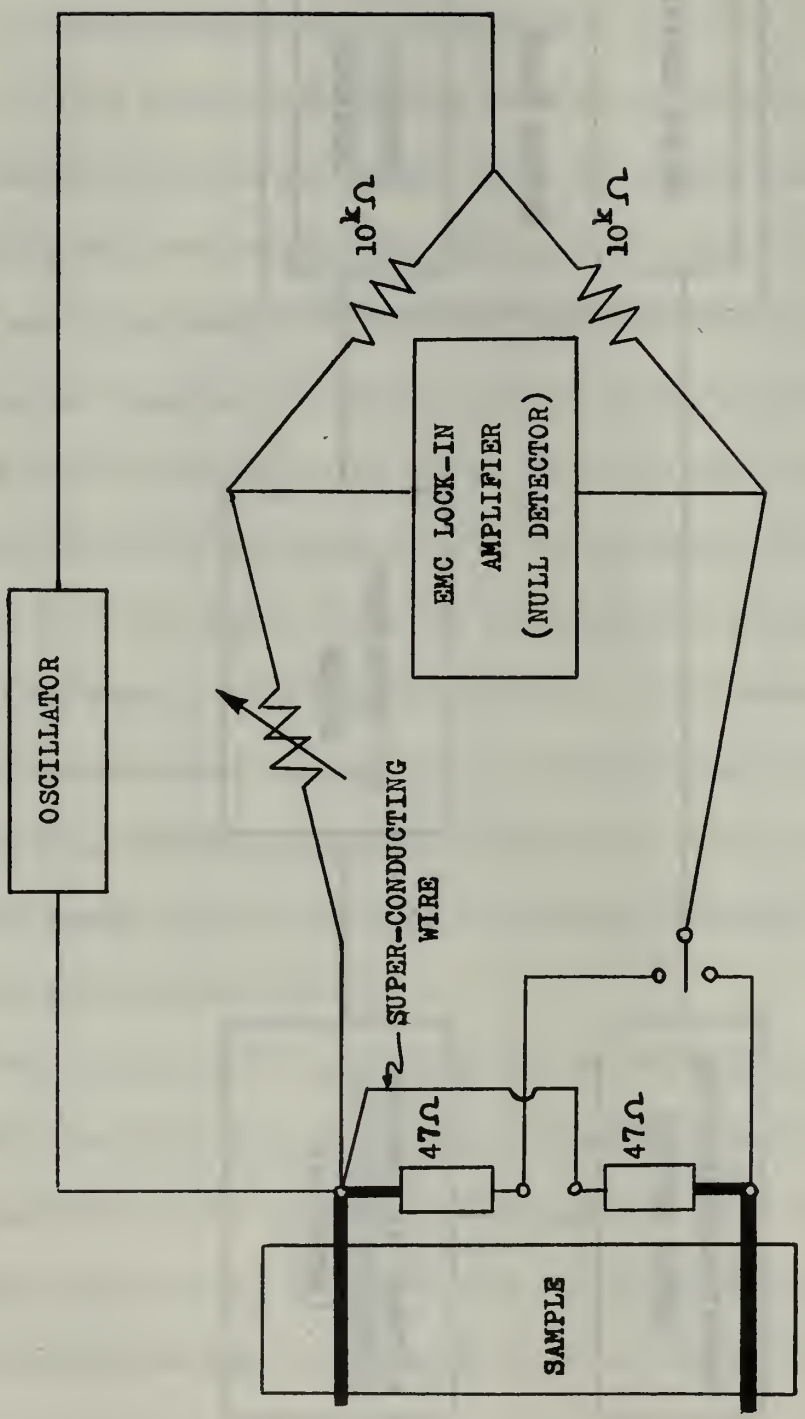

Figure 5. Measurement of carbon resistors.

despite their difference in physical location. 100-ohm resistors were initially employed as thermometers, but they were discarded in favor of the 47-ohm resistors, since they proved to have too high a resistance at the lowest temperature of interest.

Ge resistors have the characteristic of displaying a consistent value of resistance at a specified temperature even after numerous cooling and warming cycles [18]. This type of resistance thermometer was therefore selected to control the sample temperature and to provide the temperature scale against which the carbon resistors were calibrated. Prior to the first thermal conductivity run, the resistance values of the Ge resistor were calibrated against the vapor pressure of Helium. Using the 1958 temperature scale [19], the resistance values of the resistor were thus calibrated against temperature. The calibrated points were then fit in the sense of least squares to the expression

$$\frac{1}{T} = A_1 + A_2 \ln R + A_3 (\ln R)^2 + A_4 (\ln R)^3 \qquad (15)$$

where A_1, A_2, A_3 and A_4 are adjustable parameters.

Carbon resistors are less reliable than Ge resistors in displaying a consistent resistance value for a specific temperature. Therefore, the AB carbon resistors were calibrated against the Ge resistor each time that a thermal conductivity run was made.

Measurement Procedure

The procedure for determination of the thermal conductivity of the polystyrene sample was basically as follows. The bath temperature was

established by pumping on the liquid He bath. This temperature was subsequently maintained throughout the measurements. The sample was then brought to the temperature at which the thermal conductivity was to be determined by selecting that value of resistance of the Ge resistor desired and then adjusting the shield heater until a null was obtained on the detector. When the sample had reached equilibrium at the desired temperature, the values of resistance of the two AB carbon resistors and the Ge resistor were recorded. Sample equilibrium was indicated when the two carbon resistors reached constant values.

Heat was then applied to the end of the sample. The heat input to the sample was measured as voltage across the sample heater and current through it. The values of voltage and current were recorded for each heat application. The power input to the heater ranged from approximately 1.5 microwatts at the lowest sample temperature points to about 18 microwatts at the higher temperature points. When the sample came to dynamic equilibrium the values of resistances of the two AB carbon resistors were again recorded. These values gave the temperature gradient pertinent to the calculation of the thermal conductivity of the sample.

Normally, the heat input to the sample was discontinued and the sample allowed to cool to shield temperature. Heat was then reapplied to determine if data being obtained was consistent. After the data for one temperature point had been obtained, a higher sample temperature was selected and the entire procedure was repeated. Data was obtained for 14 temperature points ranging from 1.1° K to 4.5° K for each

sample radiation dose. Raw data consisting of Ge resistance values, carbon resistance values at equilibrium before and after heat application to the sample, and power input to the sample heater were inserted into a computer program for computation of the corresponding thermal conductivities. The program flow diagram is included as Appendix A. Values of thermal conductivity at various temperature points for each irradiated sample are given in Appendix B.

In addition to the data indicated above, sample warming and cooling curves resulting from application and discontinuance of heat to the sample were obtained by recording the bridge output with a Varian Associates Model G-14 Graphic Recorder. From these essentially exponential curves the dominant time constants, τ, were obtained by graphical methods for each experimental run. Time constants thus determined ranged from about 10 seconds at the lowest temperature point to about 400 seconds at the highest temperature point. Average values of $\frac{K\tau}{T^3}$ were then computed for each irradiated sample. For this geometry the specific heat capacity of the sample has been shown [20] to be given by

$$C = \frac{\pi^2 K \tau}{4L^2} \qquad (16)$$

where C is the specific heat per unit volume, K the thermal conductivity, τ the time constant, and L the sample length. Since the sample used in this experiment was tapped in one end, an effective length of the sample was computed for use in equation (16) in a manner similar to that described in previous experiments [20]. From equation (16) and

the values of $\frac{K\ell}{T^3}$ determined for each temperature point as discussed above, average values of $\frac{C}{T^3}$ were computed for polystyrene at each radiation dose. Table III contains the results. The value given in Table III for unirradiated polystyrene is taken from work by W. Reese [8].

Accuracy of Data

The determination of the resistance of the thermometers using the Wheatstone bridge circuit with lock-in amplifier as a null detector was at least accurate to .1%. The accuracy of measurement of the power supplied to the sample heater was equally as good. Further, since less than 10^{-9} watts was dissipated in the thermometers, a correction for this factor would be negligible.

Another factor which affected the accuracy of the thermal conductivity determination was the ability to maintain a constant temperature on the copper block during a measurement at a temperature point. This random error was tempered by the tendency of the two resistance thermometers to move together during changes in copper block temperature. The temperature control system was sensitive enough to prevent introduction of temperature errors exceeding 1%.

The more significant sources of error in the experiment were systematic in nature. One such source may have been imprecision in resistance-temperature calibration. Although not expected to be a serious factor for low and midrange temperatures within the $1^{\circ}K$ to $5^{\circ}K$ span, error for high temperatures may well be as large as 3%. This error is due to possible inaccuracies in evaluation of the slope of the

Sample	Total Sample Length (cm)	Effective Sample Length (cm)	Dose (Mrad)	Average Value $\frac{KT}{T^2}\left(\frac{erg}{cm-{}^oK^4}\right)$	Average Value $\frac{C}{T^3}\left(\frac{erg}{cm^3-{}^oK^4}\right)$
Unirrad.			0.0		735 ± 50
I-1	6.970	6.81	66.9	12,140	646 ± 17
I-2	6.665	6.51	226.4	10,850	631 ± 17
I-3	6.515	6.36	545.8	8,810	536 ± 11
I-4	6.037	5.88	1110.6	8,810	628 ± 13
II-1	7.050	6.91	191.5	11,370	587 ± 14

Table III

Heat Capacity Data for Irradiated Polystyrene

temperature -resistance calibration curve. The high temperature end of the calibration curve was less well determined than the lower end thereby being more uncertain for high temperatures.

The small amount of gas still present in a vacuum of about 5×10^{-7} torr may require a correction of the order of 100 ergs/sec-cm-^{o}K for the experimental values of thermal conductivity obtained. This could amount to about a 3% error at high temperatures up to a 6% error in the extreme case of lowest sample temperatures. This systematic error would tend to give high values for the thermal conductivity.

A smaller source of systematic error was the one time measurement of sample dimensions A/ℓ. Measurement of the distance between the two thermometers, ℓ, was somewhat uncertain, but the measurement should be accurate to 1%. Another systematic error was associated with sample measurements. The dimensions of the sample at liquid He temperatures were taken for computational purposes to be those at room temperature. The distance between resistance thermometers and the cross-sectional area of the sample were used in computing the thermal properties. The error thus introduced by assuming identical sample dimensions at liquid He and room temperatures might give up to 1.2% lower values for the thermal conductivity of the samples [20].

In summary, random experimental errors might introduce inaccuracies of about 1 or 2%, while the inclusion of the effects of possible systematic errors raises the uncertainty to perhaps 7 or 8%. Except for the two samples for which anomalous results were obtained, Samples I-2 and I-4, the reproducibility of thermal conductivity values for any temperature

point was easily better than 1%. More commonly, the variance of experimental values of K for any single temperature point was less than .2%. Reproducibility of thermal conductivity values for the anomalous runs was poorer, especially above 2.5°K.

It should be noted that the effect of all the foregoing systematic errors are practically the same for a sample no matter what its radiation dose. This is particularly true since the same resistance-temperature calibration curve and the same ratio of $A/_L$ were used to determine thermal conductivity values at the same sample temperature points. Then, except for small possible differences in the vacuum surrounding the sample during each run of Sample I, the effect of systematic errors on thermal conductivity values at different radiation doses should be approximately constant. This, coupled with the fact that random errors were quite small, allows a fairly accurate comparison of data between samples of differing radiation dose. In this regard, the comparative effects of radiation dose are more meaningful than the absolute values obtained.

From equation (16) it can be readily seen that the inaccuracies in experimental values of K are directly reflected in our computed values of $C/_T{}^3$. In addition to those sources of error already discussed, several more factors must be considered in evaluating the accuracy of the experimental values of $C/_T{}^3$. The rather artificial manner of correcting for the tapped end of the sample as previously discussed might well be a significant systematic error in either direction. The correction used here amounted to less than 3%.

Any possible error in boundary resistance between the sample and the copper block was neglected. The use of grease to provide good thermal contact undoubtedly reduced the magnitude of any such effect, but the degree to which an effect remained is unknown. If significant, the resulting error would tend to increase the thermal time constants thereby increasing the experimental values of $C/_T 3$. The reproducibility of the graphically obtained time constants for any given temperature point varied from as little as 3% at the lowest temperature points to as large as 20% at the highest temperature points. Temperature control of the copper block was quite important in this regard, giving rise to baseline error. Another systematic error probably resulted from neglecting the heat capacity of the 2 AB carbon resistors. The error introduced in this manner, although quite small, would tend to increase the observed thermal time constants and increase the values of $C/_T 3$.

It is pointed out that the value of $C/_T 3$ given in Table III are average values for all temperature points for a sample at a particular radiation dose. The temperature dependence of the specific heat capacity has been removed by dividing by T^3. The standard deviation given in the Table result solely from a statistical "variance from the mean" computation and do not reflect consideration of systematic errors.

III. RESULTS AND CONCLUSIONS

Thermal Conductivity

Figures 6, 7 and 8 graphically show the effects of radiation on the thermal conductivity of polystyrene. Figure 6 is a plot of thermal conductivity versus temperature for Sample I-0 (unirradiated polystyrene) and for Sample I-1 with a radiation dose of 70 Mrads. Figure 7 is a plot of thermal conductivity versus temperature for Sample II-1 and Sample I-3 with radiation doses of 190 and 545 Mrads, respectively. Figure 8 shows the anomalous data obtained from Samples I-2 and I-4 with radiation doses of 225 and 1120 Mrads, respectively. The solid curve shown in all three figures is the result of previous measurements made on unirradiated polystyrene by W. Reese [7].

Excluding the anomalous results, there appears to be no effect on the thermal conductivity of polystyrene due to irradiation and the resulting formation of crosslinks. This conclusion, drawn from Figures 6 and 7, is strengthened by the fact that as discussed previously, a close comparison of samples for the effect of different radiation doses is indeed significant since experimental random errors were small and systematic errors, though fairly large, were the same for all runs of the sample.

An unexplained observation which may have some significance, but which was not further explored, was the long time taken by all irradiated samples to reach liquid Helium temperatures when first placed in the experimental apparatus. Whereas the unirradiated

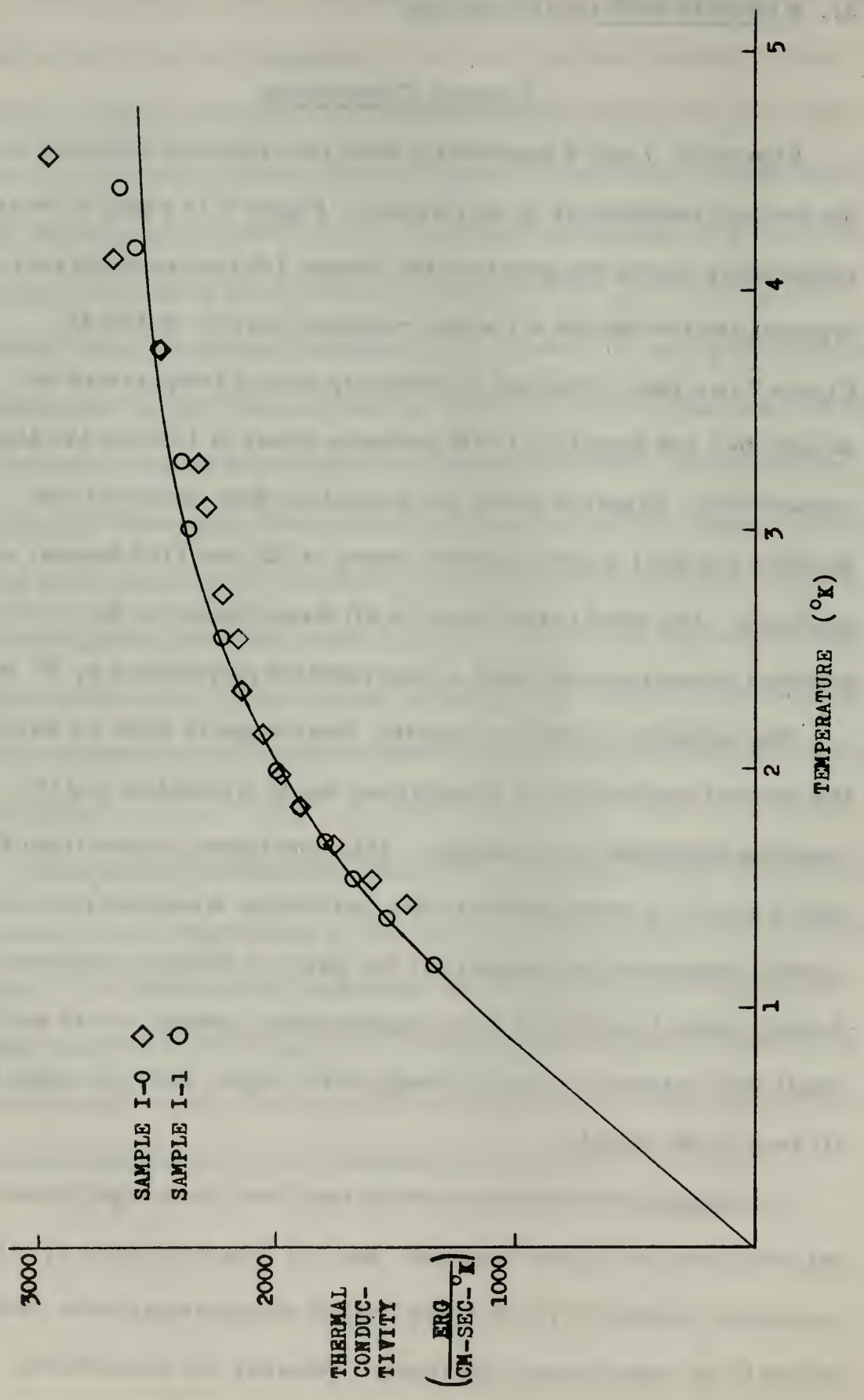

Figure 6. Thermal conductivity versus temperature for I-0 and I-1.

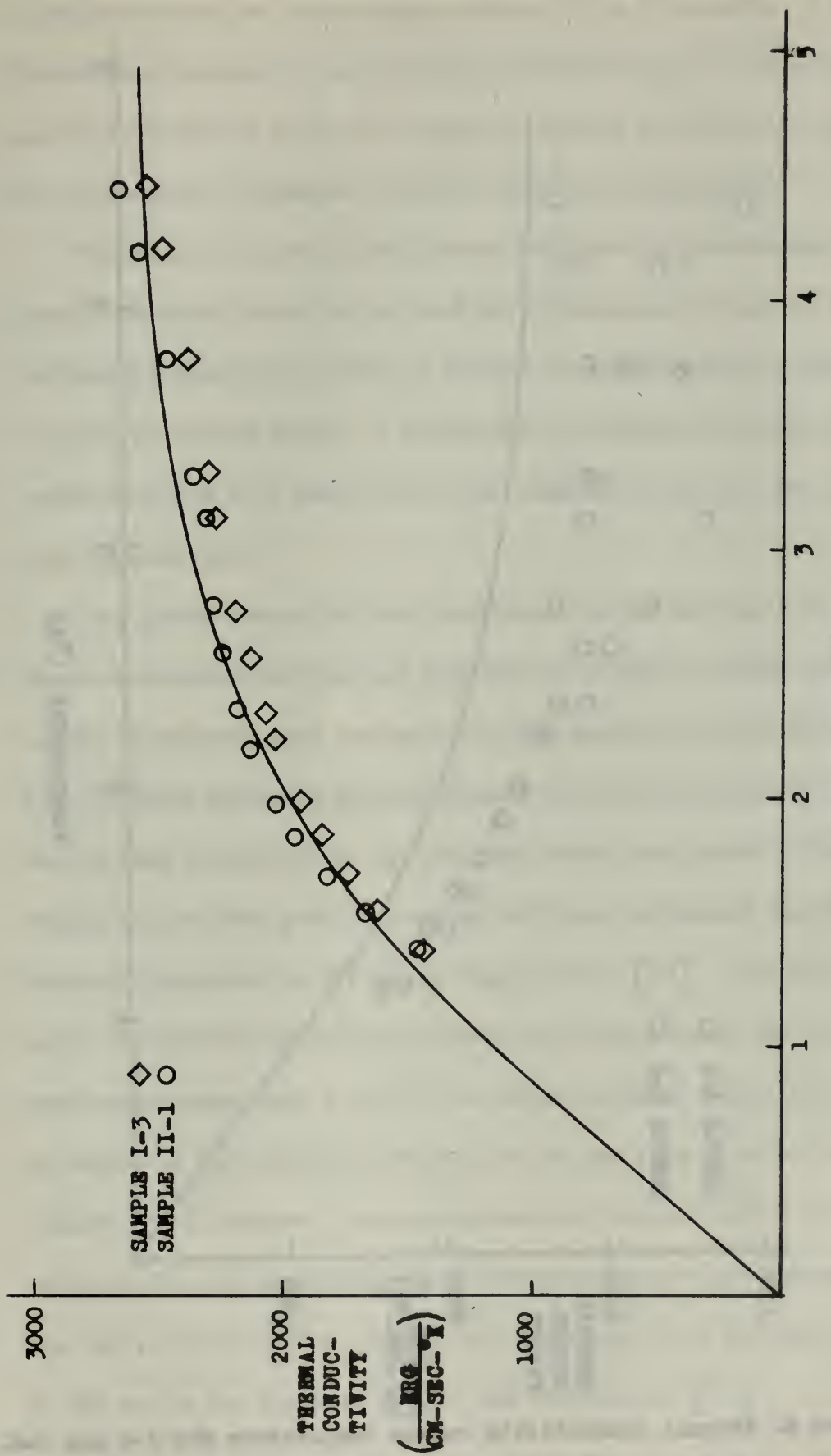

Figure 7. Thermal conductivity versus temperature for I-3 and II-1.

Figure 8. Thermal conductivity versus temperature for I-2 and I-4.

sample reached low temperatures within 15 to 20 minutes, 3 or 4 hours were required to get irradiated samples there. This observation, particularly odd in light of no apparent change in thermal conductivity due to sample irradiation, warrants further investigation.

The question immediately arises whether the anomalously high results obtained from the 2nd and 4th irradiation of Sample I as shown in Figure 8 are a real effect or merely an experimental artifact. For reasons presented below, it is felt that the effect is an experimental artifact caused by a small leak in the Indium 0-ring into the insulating high vacuum space.

The prime reason for this conclusion is the existence of a noticeable increase in shield power required to maintain shield temperature for the anomalous runs compared to that required for all the other runs. For all those series of determinations of thermal conductivity which did not lead to anomalous results, the power dissipated in the shield heater was in very good agreement with that calculated based on known thermal resistance of the brass support tube [20] . On the other hand, the power required to maintain the shield above the surrounding bath temperature was a small, but experimentally significant amount in excess of the calculated values for the two runs in which anomalous results were obtained. Assuming that the residual gas is helium, which is the only possibility at the temperatures of measurement, and that the accommodation coefficients are unity, then the heat carried by the gas in the Knudsen region will be given by [23] :

$$\dot{Q} = (4.85 \times 10^{-4})\, A\, \frac{P}{\sqrt{T}}\, \Delta T \qquad (17)$$

where $\dot{Q}$ is the heat transported by the gas in watts, A the area of the surface from which the heat is transported, P is the pressure in microns of Hg, T the temperature measured at the point of the "pressure gauge", and ΔT is the temperature difference across which the heat is transported. From the known geometry of the shield one can calculate the required gas pressure if the excess heat supplied represents gas conduction from the shield. The results of this calculation show that the excess heat transport could be accounted for by a residual gas pressure of approximately 3×10^{-6} Torr for the second irradiation and approximately 4.5×10^{-6} Torr for the fourth irradiation. These values are entirely possible in view of the prevailing external vacuum measurements at the diffusion pump.

If one assumes that there is a non-negligible amount of conduction by residual gas, and makes the slight idealization that all heat is lost to the shield and that there is a linear temperature dependence along the sample, we find, using the geometry illustrated in Figure 9, that the error in the thermal conductivity determined without correcting for gas conduction will be

$$\Delta K = (4.85 \times 10^{-4})\, \frac{P}{\sqrt{T}} \left[L + \frac{L^2}{r} - \frac{l^2}{3r} \right] \qquad (18)$$

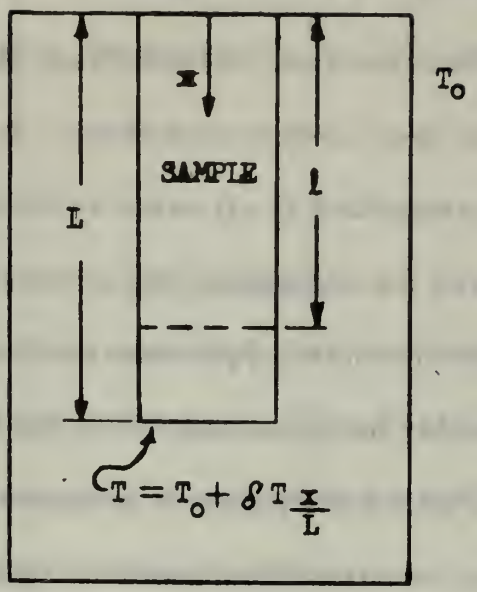

Figure 9

Model for error Calculation

where L is the length of the sample, r the sample radius, ℓ is the length over which the temperature gradient is measured, P is the pressure in microns of Hg, and ΔK is in watts per cm - ^{0}K. Inserting values appropriate for our sample, we find that the correction is approximately

$$\Delta K \simeq 350 \frac{P}{\sqrt{T}} \qquad (19)$$

Where P is expressed in units of 10^{-6} Torr and ΔK is in ergs per cm-sec-^{0}K.

As can be easily appreciated, the correction is a rather significant fraction of the measured quantities for the pressures found above. Actually, the proper pressure is rather hard to pick, since rather than choosing the pressure given above one may well argue that in the

Knudsen region $P/\sqrt{T}$ is a constant and so one should take the temperature to be that characteristic of the helium bath, the temperature used in determining the pressures quoted above. In any case, the correction is quite sizable, amounting in all cases to more than the observed differences between the anomalous and nonanomalous results. That the calculated correction is larger than that required is rather disturbing, but can most possibly be accounted for by the fact that the original model assumed a linear temperature gradient and thus neglected the additional thermal resistance encountered by lateral heat flow in the sample when cooling by gasseous conduction was present.

The foregoing calculations provide substantial argument for discounting the validity of the anomalous results. The fact that the degree of crosslinking was found to increase from irradiation to irradiation eliminates any possibility for consideration of reversal or other radical change in the effect of irradiation dose on the polymer structure as a cause for the anomalous results. The fact that both sets of anomalous data gave radical rises in thermal conductivity while a sample with an intermediate degree of crosslinking gave thermal conductivity values similar to all other runs is highly indicative that some common experimental apparatus failure may have produced the anomalous results. Certainly, the data obtained from Sample II-1 with a radiation dose comparative to that of Sample I-2 materially discredits the anomalous data as representative of a true effect of crosslinking on polystyrene. The total evidence points to the fact that crosslink formation between the polymer chains has no effect on the thermal conductivity of the

polymer and that the two anomalous runs were quite probably the result of heat leaks within the apparatus due to residual gas in the vacuum space.

Heat Capacity

The data in Table III is presented graphically in Figure 10, which is a plot of C/T^3 vs. dose. Discounting the points associated with the anomalous experimental runs, it is seen that the effect of radiation dose on the heat capacity is quite marked.

An estimate of the expected effect, based on the result of Baccaredda, et al [24], on the result of radiation on the sound velocity in polystyrene, as related to heat capacity, is indicated by the dashed line on Figure 10. This estimate is based on the relation of low temperature heat capacity to sound velocity,

$$\frac{C}{T^3} = \frac{A}{S^3} \qquad (20)$$

C being heat capacity per unit volume, T absolute temperature, S sound velocity, and A a constant containing Boltzmann's constant, and Planck's constant. The following equation relating the change in C/T^3 due to radiation may be readily derived from equation (20),

$$\left.\frac{C}{T^3}\right)_R = \left.\frac{C}{T^3}\right)_o (1 - BR) \qquad (21)$$

where B is a constant relating the change of sound velocity to radiation, and R is the radiation dose. A significant difference between the slopes

Figure 16. C/T^3 vs. Dose

of estimate based on sound velocity and the experimental line is obvious. This variance can be interpreted as due to changes in non-acoustic contributions to the heat capacity. It has been demonstrated [25] that polystyrene shows evidence of a non-acoustic contribution to heat capacity which is readily observable at liquid helium temperatures.

The reduction in C/T^3 with increasing dose indicates that the radiation has its greatest effect on the loosely bound segments of polymer chain which are primarily responsible for the excess heat capacity. One might, naively, say that radiation has the effect of inducing crystallinity in the amorphous polymer. We might also note that the reference line, based on the data of Baccaredda et al, might more appropriately be determined based on $\left(\frac{C}{T^3}\right)_{R=0} = 400$, the value reported by Reese and evaluated solely on sound velocities, rather than the intercept value $\left(\frac{C}{T^3}\right)_{R=0} = 690$ taken from Figure 10. Additionally, it must be realized that the linear extrapolation of Baccaredda's data, which was taken at 20°C, is certainly an over-simplified approach. However, the significant point here is not the value of the $\left(\frac{C}{T^3}\right)_{R=0}$, but rather the large difference in slope between the two lines.

Conclusions

The results of this investigation lead to the primary conclusion that radiation induced crosslinks in polystyrene cause no large effects on low temperature thermal conductivity. This is most easily understood

by assuming that crosslinks simply represent point imperfections relative to large phonon wavelengths at these temperatures.

Additionally, there is a reduction in the excess heat capacity of polystyrene, due to crosslink formation. This result is not particularly surprising and indicates that the major effect, on thermal properties, of crosslinks is associated with the loosely bound segments of polymer molecules.

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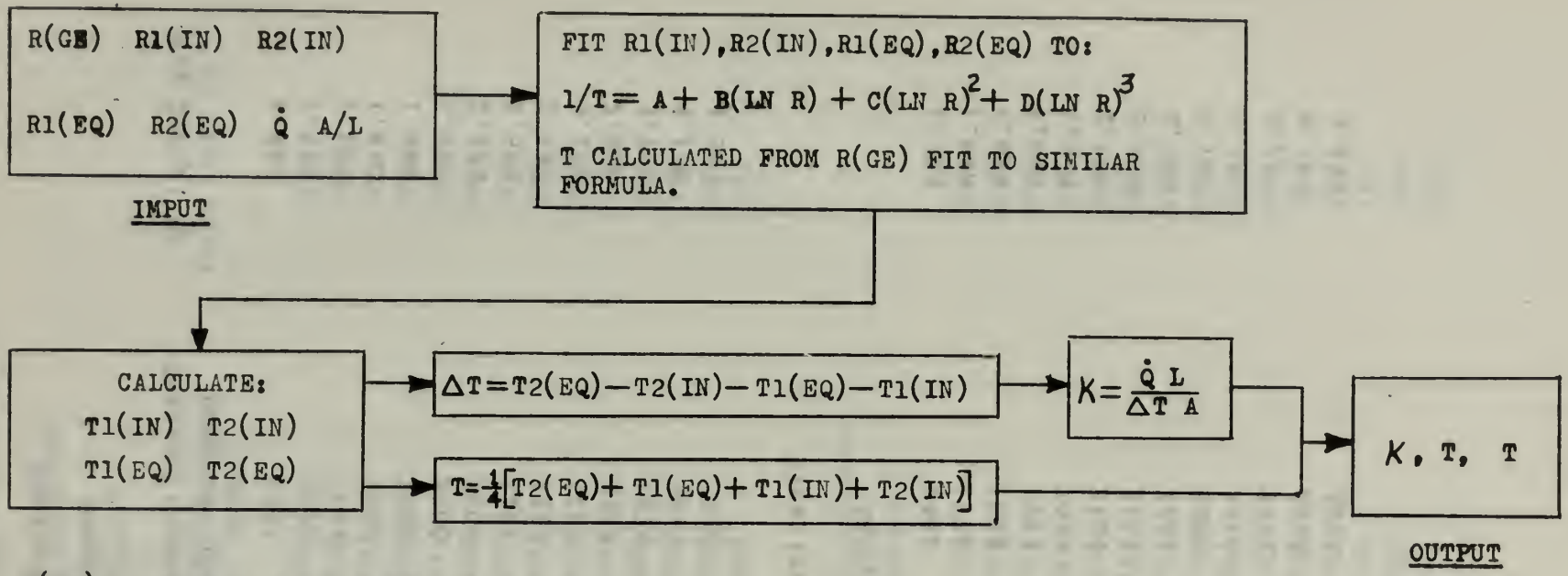

R(GE): Resistance of Germanium resistor.
R1(IN): Resistance of Nr. 1 carbon resistor with sample at equilibrium for given shield temperature.
R2(IN): Resistance of Nr. 2 carbon resistor with sample at equilibrium for given shield temperature.
R1(EQ): Resistance of Nr. 1 carbon resistor with sample at equilibrium with sample heat applied.
R2(EQ): Resistance of Nr. 2 carbon resistor with sample at equilibrium with sample heat applied.
Q̇: Power dissipated by sample heater in form of current and voltage values.
A/L: Ratio of sample cross-sectional area to length between the two carbon resistors.

APPENDIX A: Program flow for data processing.

APPENDIX B - Raw Data

Unirradiated

Sample I

Avg Temp (^{o}K)	Thermal Conductivity (erg/cm ^{o}K sec)	Temp Diff (^{o}K)
1.442	1453	.051
1.544	1602	.048
1.681	1764	.043
1.840	1902	.057
1.984	1988	.076
2.160	2060	.074
2.324	2109	.072
2.550	2161	.070
2.738	2217	.068
3.108	2284	.096
2.286	2323	.095
3.755	2474	.138
4.178	2673	.246
4.563	2942	.415

First Irradiation

Sample II

1.384	1462	.057
1.546	1778	.050
1.685	1828	.046
1.840	1953	.061
1.969	2033	.058
2.190	2134	.114
2.353	2163	.111
2.580	2244	.108
2.768	2286	.106
3.121	2316	.104
3.277	2372	.102
4.184	2598	.248
4.438	2676	.241

APPENDIX B - Raw Data

First Irradiation

Sample I

Avg Temp (^{o}K)	Thermal Conductivity (erg/cm ^{o}K Sec)	Temp Diff (^{o}K)
1.185	1345	.039
1.384	1546	.054
1.543	1691	.050
1.684	1806	.046
1.839	1916	.062
1.988	2008	.083
2.169	2095	.079
2.336	2163	.077
2.552	2235	.075
2.737	2284	.074
3.285	2406	.101
3.761	2500	.150
4.184	2604	.248
4.436	2665	.242

Second Irradiation

Sample I

1.107	1574	.034
1.376	1995	.042
1.534	2125	.039
1.672	2210	.038
1.832	2336	.051
1.978	2444	.068
2.214	2613	.143
2.319	2720	.061
2.543	2893	.058
2.732	2709	.062
3.090	2908	.083
3.270	2921	.083
3.734	2942	.127
4.155	2832	.226
4.420	2741	.234

APPENDIX B - Raw Data

Third Irradiation

Sample I

Avg Temp (^{o}K)	Thermal Conductivity (ergs/cm ^{o}K Sec)	Temp Diff (^{o}K)
1.383	1444	.058
1.545	1622	.051
1.687	1747	.048
1.841	1853	.064
1.987	1932	.086
2.235	2035	.183
2.328	2075	.080
2.556	2141	.077
2.745	2188	.077
3.122	2265	.106
3.302	2298	.105
3.764	2388	.156
4.195	2488	.258
4.448	2553	.251

Fourth Irradiation

Sample I

1.135	1723	.030
1.379	1894	.044
1.537	2069	.040
1.676	2216	.038
1.831	2367	.050
1.964	2489	.048
2.160	2642	.063
2.318	2904	.057
2.544	3063	.054
2.724	3316	.050
3.079	3663	.066
3.262	2987	.081
3.715	3523	.106
3.726	3187	.117
4.142	3410	.189
4.395	3948	.163

APPENDIX C - Recent Development

Recent investigation of current output at the NPGS linear accelerator using calorimetric methods [26] appears to have reinforced the previously mentioned speculation that the beam intensity may be higher than the values used in this work by a factor of as much as three. This development, of course, causes a number of complications in many of the interpretations of the results quoted in the thesis.

The first potential problem involves the maximum temperature which the sample reached during irradiation. Calculations, using equation (5) indicate that with a beam intensity increased by a factor of three, the center of the sample might reach a temperature of 51°C. Consequently, this increase in temperature poses no major complication, since the sample would still remain below the softening temperature of polystyrene. (However, the margin for safety is greatly reduced).

With regard to the crosslinking determinations there are a number of complications. The first consideration involves the value of μ, which is already subject to a fairly large uncertainty. In order to have consistent results a value $\mu = .2$ would be necessary. This, however, would cause the gel dose for this material to be approximately 180 M rads which is entirely inconsistent with the W.A.M.W. of the polystyrene sample.

The only remaining possibility involves the validity of using $G = .05$ for relativistic electrons. In order to make all the results,

(related to polymer characterization), agree, a G-factor of approximately .016 would be necessary. Since previous experiments related to crosslinking in polystyrene have all used low energy radiation, the variation of the G-factor certainly must be considered as a possibility.

In spite of the uncertainties mentioned above, the basic conclusion of this study is essentially unaffected.

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13. ABSTRACT

Measurements of the thermal conductivity of polystyrene, irradiated with 80 Mev electrons, were made in the temperature range of 1.0°K to 5.0°K. Additionally, an estimate of the corresponding heat capacities was made. Samples irradiated received total doses of approximately 70, 200, 230, 550, and 1120 M rads.

There was no observable effect, due to radiation induced crosslinks, on the thermal conductivity. The heat capacity, however, showed a marked decrease with increased dose. This effect is attributed to a reduction in the "excess" heat capacity of polystyrene, indicating that crosslinking has its greatest affect on the loosely bound polymer segments.

Polymer characterization was accomplished by use of intrinsic viscosity and equilibrium swelling techniques.

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14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Thermal Conductivity						
Heat Capacity						
Polystyrene						
Low Temperatures						
Radiation Damage						
Crosslinking						